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Moisture Sorption Isotherms of Pigeonpea (*Cajanas cajan*) Grain and its Dehulled Splits (Dhal)

R.K. Vishwakarma, R.K. Goyal and V.K. Bhargav
Central Institute of Post Harvest Engineering and Technology, PAU Campus,
Ludhiana 141 004, Punjab, India

Abstract: Moisture sorption isotherms of pigeonpea grain (*Cajanas cajan*) and dehulled splits of pigeonpea (dhal) at 10, 20, 30, 40 and 50°C were derived. The sorption data were treated according to many well-known sorption isotherm equations. The goodness of fit was evaluated on the basis of criteria such as the residual sum of squares, standard errors of estimates and mean relative deviation. It was found that the modified Chung-Pfost equation was the most satisfactory model for representation of the EMC data for pigeonpea grain up to 80% ERH. Modified Henderson equation was the most satisfactory model for representation of the EMC data for pigeonpea dhal.

Key words: Dehulling, moisture isotherms, pigeonpea, processing and storage

INTRODUCTION

Pigeonpea (*Cajanas cajan*) is one of the important pulse crops of India and contributes 20% to the total production of all pulses. India accounts for 90% of the total world production of pigeonpea. It is consumed as dehulled splits (dhal) and is one of the important constituents of diet especially vegetarian population of India as a source of protein. Before cooking or other processing operations, it is necessary to remove the fibrous seed coat (hull) of pigeonpea in order to reduce fiber content and improve palatability. The hull of pigeonpea adheres tightly to the cotyledons through a gummy layer, which qualifies it as difficult to mill pulse. Moisture content plays significant role in dehulling of pulses.

The control of moisture content of foods during processing and storage is very important it affects food reactions and food quality. In this respect the moisture sorption isotherm is an extremely important tool in food engineering because it can be used to predict changes in food stability and to select appropriate packaging materials and ingredients. It is also necessary to know the relationship between the Equilibrium Moisture Content (EMC) and Equilibrium Relative Humidity (ERH) of pigeonpea grain and dhal at a given temperature. Many researchers have developed theoretical or empirical based EMC/ERH equations. Van den Berg and Bruin (1981) have compiled more than 200 EMC/ERH equations. Despite the availability of the large number of equations, no single equation is found to have ability to describe accurately the EMC/ERH relationships for different grains over a broad range of relative humidity and temperature (Sun and Woods, 1993). Therefore, for a specific crop and processed product, there is a need to search for the most appropriate EMC/ERH equation (Chen and Morey, 1989; Sun and Woods, 1994a,b; Sun and Byrne, 1998).

There are many works on moisture sorption isotherms of foods over the last two decades. Some of these works are related to the determination of moisture sorption isotherms and some are related to the mathematical formulation to represent the moisture sorption isotherms (Ayrannci, 1995; Debnath *et al*., 2002; Maskan and Gogus, 1997; Menkov, 2000). However, information available on

Corresponding Author: R.K. Goyal, Central Institute of Post Harvest Engineering and Technology, PAU Campus, Ludhiana 141 004, Punjab, India Tel: +91 161 2808669 Fax: +91 161 2808670

comparing and selecting EMC/ERH equations for pigeonpea grain and dhal is very limited. Al-Muhtaseb *et al*. (2002) reviewed the moisture sorption characteristics of food products and discussed applicability of various mathematical models. Chen (2003) reported the moisture sorption isotherms of pea seeds with different treatments and adopted some of the mathematical models to the isotherm data and found that modified Henderson equation be an adequate model. The GAB model, which is in general considered as one of the best models for moisture sorption isotherms of foods (Labuza, 1984), was not found to be a good model when applied to sorption data of pea seeds. Ayranci and Duman (2005) reported the moisture sorption isotherms of cowpea, powdered cowpea and protein isolates of cowpea at 10, 20 and 30°C. GAB model was the most satisfactory model for representation of sorption data. Swami *et al*. (2005) studied the moisture sorption isotherm of black gram nuggets at different temperature and relative humidity conditions and fitted to GAB model.

The purpose of the present study is to determine the moisture sorption isotherms for pigeonpea grain and dehulled splits of pigeonpea (dhal) at five temperatures, 10, 20, 30, 40 and 50°C by varying the relative humidity. Five empirical equations based on the experimental data were applied in an attempt to better reproduce the equilibrium moisture content.

MATERIALS AND METHODS

Pigeonpea grain (variety UPAS-120) was purchased from local market. Dehulled splits (dhal) from pigeonpea grain was prepared using Pantnagar mini dhal mill (capacity: 50 kg h^{-1}, carborundum grade: 24). Initial moisture content of pigeonpea grain was determined as 9.5% (d.b.) and that of dhal was 9.1% (d.b.). Moisture content of dhal was adjusted to 9.5% (d.b.). Temperature range of 10-50°C and relative humidity range of 38-95% was selected because this range is commonly prevalent in all parts of India. The equilibrium moisture content for adsorption of pigeonpea grain and dhal were determined by static gravimetric technique based on isopiestic transfer of water vapour (Suthar and Das, 1997). Saturated salt solutions of $CaCl_26H_2O$, $Ca(NO_3)_2$, NH_4NO_3, NH_4Cl, KNO_3, KCNS, NaBr, $(NH_4)_2SO_4$, $Mg(NO_3)26H_2O$, $NaNO_2$, CH_3COONa, NaCl, KCl and K_2SO_4 were prepared to obtain constant relative humidity environments. All salts were of reagent grade. Water activities of saturated solutions of above salts at different temperatures were taken from Labuza (1984).

Controlled humidity environment was generated in closed chambers (desiccators). The desiccators were kept in temperature-controlled cabinets at 10, 20, 30, 40 and 50±1°C replicated thrice. The samples were weighed in the respective moisture boxes in a single layer then placed in the desiccators. Each desiccator had respective saturated salt solutions to obtain constant relative humidity environment. Samples were weighed with digital balance (least count: 0.0001g, Citizen, Japan) after every two days. Samples were equilibrated for approximately 28 days, as evidenced by constant values (±0.001 g) of three consecutive weighments. The moisture content of each sample was determined by hot air oven drying method (AOAC, 1984).

Mathematical Equations to Predict Adsorption Isotherms and Fitting Methods

In a study, Chen (1988) identified that the modified Henderson, modified Chung-Pfost, modified Halsey, modified Oswin and Chen-Clayton equations are commonly used to fit the EMC/ERH data of grains and seeds. The Modified Henderson Equation (MHEE) (Thompson *et al*., 1968) and the modified Chung-Pfost Equation (MCPE) (Pfost *et al*., 1976) are recommended by the ASAE Standard (ASAE, 1995). In the 1996 revision of the ASAE standard (ASAE, 1997), the modified Oswin equation (MOSE) (Oswin, 1946) and the modified Halsey equation (MHAE) (Iglesias and Chirife, 1976) were added as the recommended equations. Chen Clayton equation (MCCE) (Chen and Clayton, 1971) was also taken to fit the EME/ERH data to observe its applicability for pigeonpea. Each of the equations has three parameters (except MCCE which has four parameters) and each can be solved explicitly for relative humidity as a function of temperature and moisture content, or for moisture content as a function of temperature and relative humidity. Therefore the following equations were chosen for the current study.

- Modified Henderson equation (MHEE) can be written as:

$$1\text{-}R_H = \exp[-C_1 \ (T+C_2)M^{C_3}] \tag{1}$$

$$M = \left(\frac{\ln(1-R_H)}{-C_1(T+C_2)}\right)^{1/C_3} \tag{2}$$

- Modified Chung-Pfost equation (MCPE) can be written as:

$$R_H = \exp\left(-\frac{C_1}{(T+C_2)}\exp(-C_3M\right) \tag{3}$$

$$M = C_1 \text{-} C_3 \ln[-(T+C_2)\ln(R_H)] \tag{4}$$

- Modified Oswin equation (MOSE) can be written as:

$$R_H = \left(\frac{1}{[1+(C_1+C_2T)/M]^{C_3}}\right) \tag{5}$$

$$M = (C_1+C_2T)\left(\frac{(1-R_H)}{R_H}\right)^{-1/C_3} \tag{6}$$

- Modified Halsey equation (MHAE) can be written as:

$$R_H = \exp[-\exp(C_1+C_2T)M^{-C_3} \tag{7}$$

$$M = \exp(C_1+C_2T)[-\ln(RH)]^{-1/C_3} \tag{8}$$

- Chen-Clayton equation (MCCE) can be written as:

$$R_H = \exp[-C_1T^{C_2} \ (\exp(-MC_3T^{C_4} \ )] \tag{9}$$

$$M = \frac{-1}{C_3T^{C_4}}\ln\left(\frac{\ln(R_H)}{-C_1T^{C_2}}\right) \tag{10}$$

In Eq. 1-10, R_H is the equilibrium relative humidity in decimal, M is the equilibrium moisture content in percent dry basis, T is the temperature in °C and C_1, C_2, C_3 and C_4 are equation coefficients.

In Eq. 1-10, the coefficients C_1, C_2, C_3 and C_4 for a set of EMC/ERH data can be obtained by using the non-linear least-squares regression methods. To select the most appropriate equation, SYSSTAT version11 software was used. The following three quantitative error parameters were used for comparison of equilibrium moisture content and equilibrium relative humidity isotherm equations. The Residual Sum-of-Squares (RSS) is an important error parameter during non-linear curve fitting process. The RSS is defined as follows:

$$RSS = \sum_{i=1}^{n} (M - M_S)^2 \tag{11}$$

where Ms is the simulated value of M.

The standard error of estimate (SEE) indicates the fitting ability of a model to a set of data (Sun and Byrne, 1998). The SEE shows the deviation of the dependent variable M and is given by:

$$SEE = \sqrt{\frac{\sum_{i=1}^{n} (M - M_S)^2}{df}} \tag{12}$$

where df is degree of freedom.

The SEE value only indicates the fitting ability of an equation; it cannot provide a direct visualization of goodness of fit of the equation. The Mean Relative Deviation modulus (MRD) is therefore used to describe the goodness of fit of an equation (Sun and Byrne, 1998). The MRD gives an idea of the mean deviation of the measured data from the predicted data. Therefore, the smaller the MRD value, the better the goodness-of-fit. It is expressed as:

$$MRD = \frac{1}{n} \sum_{i=1}^{n} \frac{|M - M_S|}{M} \tag{13}$$

Similar error parameters are also used for comparison of equilibrium relative humidity.

DISCUSSION

A set of 24 experiments was performed each to investigate the influence of the main operating parameters on the EMC of pigeonpea grain and dhal. Table 1 reports the experimental EMC data (d.b.) obtained by varying the values of relative humidity and temperature, respectively. The moisture sorption isotherms for pigeonpea grain and its dhal at 10, 20, 30, 40 and 50°C are shown in Fig. 1, respectively. In general all the isotherms showed characteristics of type III isotherm according to the classification of Al-Muhtaseb *et al*. (2002). Foods rich in soluble components have been found to show this type of isotherm.

It is seen from Fig. 1 that equilibrium moisture content of dhal is slightly higher than that of grain at lower equilibrium relative humidity (less than 80%) conditions. This indicates that few additional sites become accessible for water sorption in pigeonpea dhal (after dehulling and splitting of pigeonpea grain). Dehulling and splitting also increases surface area and hence EMC of dhal is slightly higher than that of grain. In order to verify the difference between EMC of pigeonpea grain and that of dhal, student t-test for mean was carried out. It suggests that the difference in mean is non-significant at 5% level of significance ($p>0.05$). Effect of relative humidity on EMC is more pronounced than temperature. EMC of both pigeonpea grain and dhal is decreasing with temperature, which is a known phenomenon for all food materials. At higher temperature (above 30°C) and higher ERH conditions (above 80%) the EMC of grain is more than that of dhal. This indicates that presence of hull in pigeonpea grain acts as barrier to water vapors to some extent and hence EMC of grain is slightly higher. It is difficult to compare the results with the literature since no work on comparing the EMC of pigeonpea grain and dhal is available. However, Ayranci and Duman (2005), compared the EMC of cowpea grain, its powder and protein isolates. They observed no difference in EMC of cowpea and its powder but the EMC of protein isolates was lower than cowpea.

Table 1: Experimental conditions and equilibrium moisture content for pigeonpea grain and dhal

		EMC % (d.b.)	
Temperature (°C)	Relative humidity (%)	Pigeonpea grain	Pigeonpea dhal
10	38.0	10.08	11.73
10	59.0	14.68	15.81
10	67.1	16.58	17.30
10	81.0	24.52	22.00
10	95.5	32.73	34.57
20	49.0	11.96	12.13
20	59.2	14.00	14.77
20	72.6	16.01	18.06
20	81.6	19.95	21.08
20	93.2	32.22	32.68
30	51.4	11.89	11.89
30	63.3	13.99	14.48
30	71.4	14.90	17.34
30	80.0	18.67	18.76
30	90.7	31.41	29.17
40	49.2	11.28	11.46
40	61.8	13.31	14.19
40	67.7	14.51	16.48
40	81.7	18.30	18.13
40	87.9	30.04	28.97
50	46.3	9.28	11.33
50	74.5	13.96	16.46
50	79.1	17.37	17.72
50	95.8	31.49	28.42

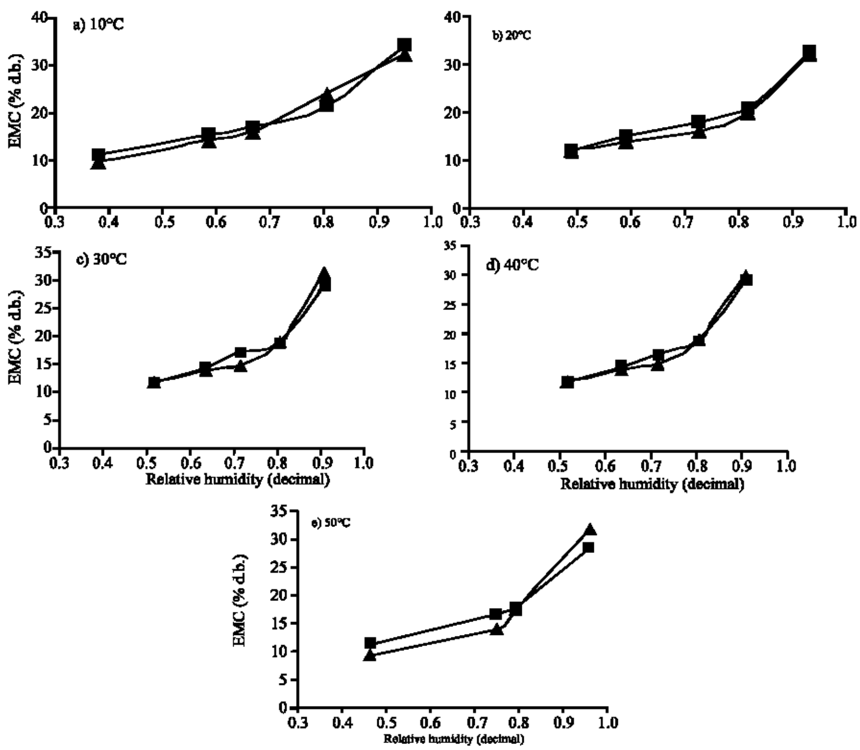

Fig. 1: Moisture sorption isotherms of pigeonpea grain (▲) and pigeonpea dhal (■) at 10, 20 30 40 and 50°C

Fitting EMC data to five isotherms equations

The EMC data were fitted to Eq. 1-10. The best fitted coefficients of ten isotherm equations are listed in Table 2 for pigeonpea grain and dhal, with the three error parameters RSS, SEE and MRD, which determine the performance of each equation. On analyzing Table 2, it can be seen that the error parameters for both equilibrium moisture contents and equilibrium relative humidities obtained with all five equations were similar. However, the RSS for EMC prediction were high.

In order to check the error points, EMC-ERH relationship for observed values and predicted values from each equation was plotted at different temperatures for pigeon grain and dhal separately (Fig. 2). It can be observed from Fig. 2 that all equations are predicting EMC closely at lower ERH but at higher ERH, the prediction is not good. The predicted values at higher ERH (above 80%) and lower temperatures (up to 30°C) are slightly higher than that of observed values. But in temperature range 40-50°C and ERH above 80%, the predicted values are lower than that of observed values. Thus, these equations are predicting EMC for ERH up to 80% in the range of observed one. Comparing error parameters, the modified Chung-Post equation gives the smallest error parameters followed by Chen-Clayton equation. The results in Table 2 and predicted values shown in Fig. 2 confirm that modified Chung-Pfost equation is the most suitable equation for prediction of adsorption EMC of pigeonpea grain up to 80% ERH.

Similarly for pigeonpea dhal, EMC-ERH relationship for observed values and predicted values from each equation was plotted at different temperatures (Fig. 3). It can be observed from Fig. 3 that all equations are predicting EMC better than grain at lower ERH (up to 80%) but at higher ERH the prediction is not good. Similarly in temperature range 40-50°C and ERH above 80%, the predicted values are lower than that of observed values. Thus, these equations are predicting better than grain for ERH up to 80%. Comparing error parameters, the modified Henderson equation gives the smallest

Table 2: The best fitted coefficients of ten equations and the error parameters for the experimental data set defined in Table 1

Model		Eq. No.	Equation parameters C_1	C_2	C_3	C_4	RSS[a]	SEE[b]	MRD[c]
For pigeonpea grain									
	MHEE	(1)	0.000175	88.114	1.469	-	0.0290	0.0372	0.03905
	MCPE	(3)	308.845	68.066	0.137	-	0.0280	0.0365	0.03583
$R_H = f(M,T)$	MOSE	(5)	13.155	-0.062	2.598	-	0.0170	0.0285	0.03243
	MHAE	(7)	5.002	-0.011	2.083	-	0.0190	0.0301	0.03945
	MCCE	(9)	3.176933	0.01114	0.0869	0.14549	0.0265	0.0355	0.03696
	MHEE	(2)	0.000123	210.789	1.326	-	101.4430	2.1979	0.08162
$M = f(R_H,T)$	MCPE	(4)	47.371	82.794	8.399	-	97.0590	2.1499	0.07722
	MOSE	(6)	13.092	-0.037	2.873	-	122.6000	2.4162	0.07119
	MHAE	(8)	2.462	-0.003	2.613	-	137.6640	2.5604	0.07993
	MCCE	(10)	8.0071	-0.3559	0.1449	-0.0614	97.9688	2.1599	0.08099
For pigeonpea Dhal									
	MHEE	(1)	0.000081	106.825	1.6613	-	0.0218	0.0322	0.03471
	MCPE	(3)	433.224	76.590	0.1454	-	0.0185	0.0297	0.03223
$R_H = f(M,T)$	MOSE	(5)	13.8652	-0.5100	2.8692	-	0.0152	0.0269	0.03205
	MHAE	(7)	5.75573	-0.0095	2.3255	-	0.0163	0.0279	0.03357
	MCCE	(9)	6.208849	-0.1229	0.1231	0.05305	0.0163	0.0278	0.02911
	MHEE	(2)	0.000109	129.608	1.4899	-	60.2372	1.6936	0.05745
$M = f(R_H,T)$	MCPE	(4)	43.9145	65.3988	7.6328	-	64.4767	1.7522	0.05638
	MOSE	(6)	1.4494	-0.5461	3.1752	-	70.2900	1.8295	0.04878
	MHAE	(8)	2.57466	-0.0041	2.8804	-	82.1435	1.9778	0.05704
	MCCE	(10)	4.14319	-0.0567	0.1035	0.07595	65.0170	1.7596	0.05297

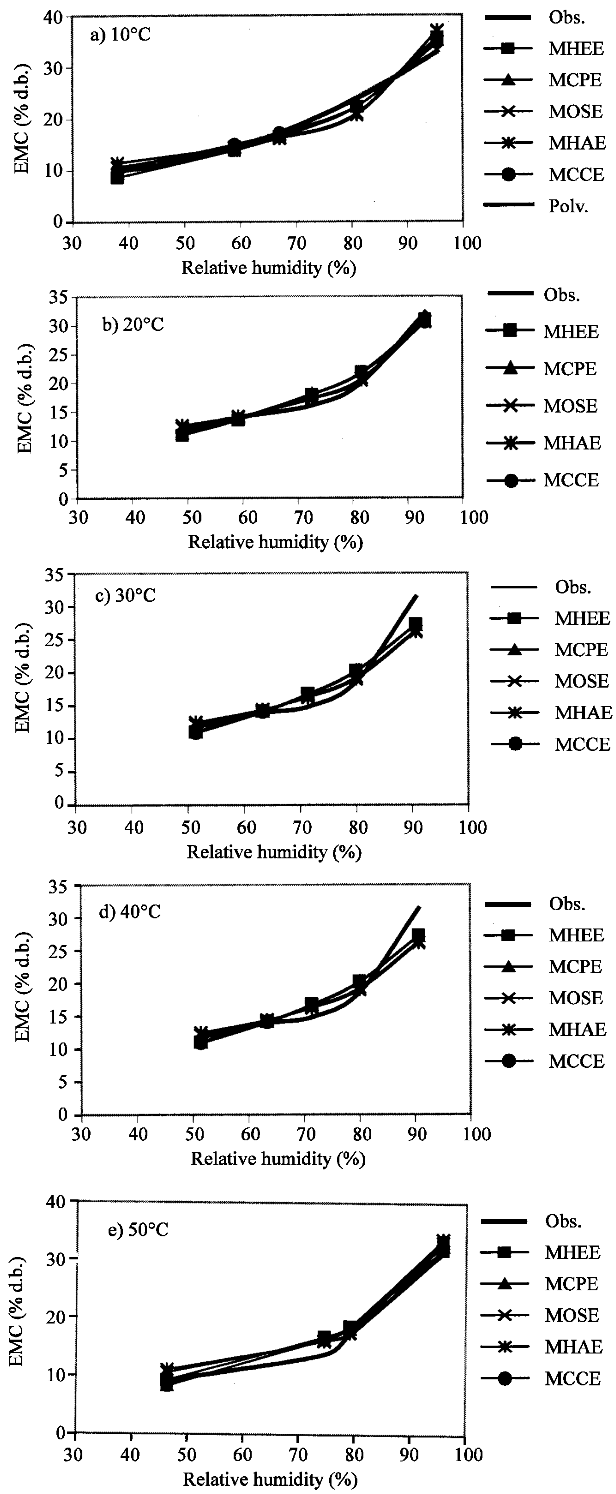

Fig 2: Comparison between the adsorptive isotherms at 10, 20 30 40 and 50°C predicted by five different models and the experimental data for pigeonpea grain

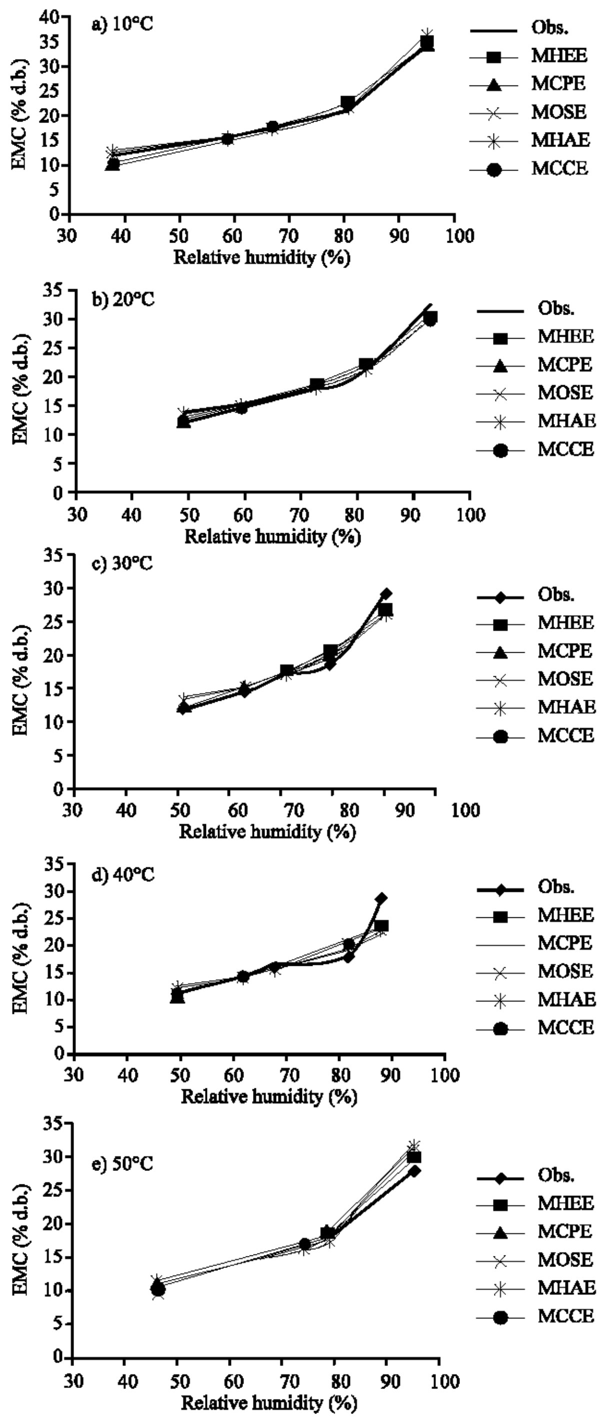

Fig 3: Comparison between the adsorptive isotherms at 10, 20 30 40 and 50°C predicted by five different models and the experimental data for pigeonpea dhal

error parameters followed by modified Chung-Post equation.. The results in Table 2 and predicted values shown in Fig. 3 confirm that modified Henderson equation is the most suitable equation for prediction of adsorption EMC of pigeonpea dhal up to 80% ERH followed by modified Chung-Pfost equation.

CONCLUSIONS

A set of experiments was performed to obtain Equilibrium Moisture Content (EMC) values for pigeonpea grain and dhal at different relative humidities in the range of temperature from 10-50°C. Five empirical models were evaluated for reproducing the experimental results and the effect of temperature and relative humidity on pigeonpea grain and dhal. A regression analysis indicates that the modified Chung-Pfost equation as the best for pigeonpea grain among the five investigated ones for predicting EMC up to 80% ERH, whereas modified Henderson equation was found best equation for pigeonpea dhal.

REFERENCES

AI-Muhtaseb, A.H., W.A.M. Mcminn and T.R.A. Magee, 2002. Moisture sorption isotherm characteristics of food products: A Rev. Trans Chem. E, 80 (Part C), pp: 118-128.

AOAC., 1984. Official methods of analysis. Association of Official Agricultural Chemists, Washington D.C.

ASAE D245.4, 1995. Moisture Relationship of Grains, ASAE Standards 42nd Edn., Michigan, USA: St. Josaph.

ASAE D245.5, 1997. Moisture Relationship of Plant-Based Agricultural Products, ASAE Standards 44th Edn., Michigan, USA: St. Joseph.

Ayrannci, E., 1995. Equilibrium moisture characteristics of dried eggplant and okra. Nahrung. 39: 228-233.

Ayranci, E. and O. Duman, 2005. Moisture sorption isotherms of cowpea (*Vigna unguiculata* L. Walp) and its protein isolates at 10, 20 and 30°C. J. Food Eng., 70: 83-91.

Chen, C.S. and J.T. Clayton, 1971. The effort of temperature on sorption isotherms of biological materials. Trans. ASAE, 14: 927-929.

Chen, C.C., 1988. A study of equilibrium relative humidity for yellow-dent corn kernels. Ph.D. Thesis. University of Minnesta, St. Paul.

Chen, C.C. and R.V. Moery, 1989. Comparison of four EMC/ERH equations. Trans. ASAE., 32: 983-990.

Chen, C., 2003 Moisture sorption isotherms of pea seeds. J. Food Eng., 58: 45-51.

Debnath, S., J. Hemavathy and K.K. Bhat, 2002. Moisture sorption studies on onion powder. Food Chem., 78: 479-480.

Iglesias, H.A. and J. Chirife, 1976. Prediction of effect of temperature on water sorption isotherms of food materials. J. Food Technol., 11: 109-116.

Labuza, T.P., 1984. Moisture Sorption: Practical Aspects of Isotherm Measurement and Use. Minneapolis, MN: American Association of Cereal Chemists.

Maskan, M. and F. Gogus, 1997. The fitting of various models to water sorption isotherms of pistachio nut paste. J. Food Eng., 33: 227-237.

Menkov, N.D., 2000. Moisture sorption isotherms of chickpea seeds at several temperatures. J. Food Eng., 45: 189-194.

Oswin, C.R., 1946. The kinetics of package life III Isotherm. J. Chem. Ind. London, 65: 419-421.

Pfost, H.B., S.G. Maurer, D.S. Chung and G.A. Milliken, 1976. Summarizing and reporting equilibrium moisture data for grains. ASAE Paper No. 76-3520, St. Josaph, Michigan, USA.

Sun, Da-Wen and J.L. Woods, 1993. The moisture content/relative humidity equilibrium relationship of wheat. A review. Drying Technol., 11: 1523-1551.

Sun, Da-Wen and J.L. Woods, 1994a. Low temperatures moisture transfer characteristics of barley thin-layer models and equilibrium isotherms. J. Agric. Eng. Res., 59: 273-283.

Sun, Da-Wen and J.L. Woods, 1994b. The selection of sorption isotherm equations for wheat based on the fitting of available data. J. Stored Prod. Res., 30: 27-43.

Sun, Da-Wen and C. Byrne, 1998. Selection of EMC/ERH isotherm equations for rapeseed. J. Agric. Eng. Res., 69: 307-315.

Suthar. S.H. and S.K. Das, 1997. Moisture sorption isotherms for Karingda (*Citrullus lanatus*) (Thumb) Manst seed kernel and hull. J. Food Process Eng., 20: 349-366.

Swami, S.B., S.K. Das and B. Maiti, 2005. Moisture sorption isotherms of black gram nuggets (*bori*) at varied temperatures. J. Food Eng., 67: 477-482.

Thompson, T.L., R.M. Peart and G.H. Foster, 1968. Mathematical simulation of corn drying-a new model. Transa. ASAE, 24: 582-586.

Van den Berg, C. and S. Burin, 1981. Water activity and its Estimation in food Systems: Theoretical Aspects. In: Rockland, L.B. and G.F. Stewart (Eds.), Water activity: Influences on food quality. New York: Academic Press, pp: 1-61.